

EUROPEAN PATENT APPLICATION

Application number: 89312390.1

Int. Cl.⁵: **C09D 133/14, C08F 220/28,**
/(C08F220/28,220:32,220:06,
220:10)

Date of filing: 29.11.89

Priority: 09.12.88 US 281652

Date of publication of application:
13.06.90 Bulletin 90/24

Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

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Ambient temperature curing polymer compositions.

The invention relates to a coating composition which cures at ambient temperatures which comprises an aqueous dispersion having a pH of 8.5 to 10 of a copolymer of a) acetoacetoxyethyl acrylate or methacrylate, b) glycidyl acrylate or methacrylate, c) an ethylenically unsaturated polymerisable acid, and d) a monomer other than a), b) and c) and copolymerisable therewith, wherein the weight ratio a) to b) is less than or equal to 0.5/1 or greater than 1.5/1 and the weight ratio of b) to c) is greater than 1.5/1, the total weight percent of a), b) and c) in the copolymer is from 8 to 60, the weight percent of c) is from 1.5 to 20 and the weight percent of d) is from 40 to 92.

EP 0 372 804 A2

AMBIENT TEMPERATURE CURING POLYMER COMPOSITIONS

The invention relates to a coating composition which cures at ambient temperatures.

Coating compositions which cure under ambient conditions have long been known. The earliest such coating compositions were based on drying oils which cure by air oxidation. More recently developed compositions are those based on the epoxide-carboxylic acid reaction, isocyanate-moisture reaction, 5 polyaziridine-carboxylic acid reaction, and activated methylene-unsaturated carboxylic acid reaction.

US-A-3,554,987 discloses film-forming interpolymers of acrylic acid, acetoacetoxyethyl methacrylate and monomers copolymerised therewith.

US-A-4,408,018 discloses mixing polymers containing pendant acetoacetate moieties with polyacrylates which contain more than one unsaturated acrylic group and curing the mixture through Michael additon 10 using a strong base as catalyst.

Crosslinking through Michael addition is also described in EP-A-227,454 wherein compounds containing a plurality of pendant acetoacetate groups are blended with compounds containing a plurality of ethylenical-ly unsaturated acrylic groups and are cured with the addition of a strong base or an organometallic compound.

15 ZA-A-85-2044 describes coating compositions curable at ambient temperatures made from a composition containing a plurality of activated methylene groups and ethylenically unsaturated carbonyl groups.

In an article by A. Noomen, entitled "Ambient Temperature Curable Coatings Based on Two-Pack Binders", Organic Coatings Conference, Athens, Greece - June, 1987, coating compositions which cure through the Michael addition reaction of acetoacetate-ketimine groups and acrylic-malonate groups are 20 discussed.

Thermosetting coating compositions based on the epoxide-carboxylic acid reaction are disclosed in US-A-3,305,601, US-A-4,028,294 and EP-A-226,171. Due to the ever increasing demand for decorative and protective coatings which will withstand a wide variety of uses and will hold up under all kinds of environmental conditions, there is continuing research in utilizing various reactants in coating compositions.

25 The invention provides a coating composition which comprises an aqueous dispersion having a pH of 8.5 to 10 of a copolymer of a) acetoacetoxyethyl acrylate or methacrylate, b) glycidyl acrylate or methacrylate, c) an ethylenically unsaturated polymerisable acid, and d) a monomer other than a), b) and c) and copolymerisable therewith, wherein the weight ratio a) to b) is less than or equal to 0.5/1 or greater than 1.5/1 and the weight ratio of b) to c) is greater than 1.5/1, the total weight percent of a), b) and c) in the 30 copolymer is from 8 to 60, the weight percent of c) is from 1.5 to 20 and the weight percent of d) is from 40 to 92.

When the composition is applied as a coating to a substrate, the coating cures at room temperature to a thermoset state.

35 The acetoacetoxyethyl (meth)acrylate monomer a) used in the composition of this invention can be made by the reaction of diketene with hydroxyethyl (meth)acrylate. The acetoacetoxyethyl group contains a methylene group between the two carbonyls and is said to be an "active" methylene group. Such groups are capable of Michael addition across double bonds and can react with epoxide groups.

The glycidyl (meth)acrylate monomers b) used in the composition of this invention are well known commercially available monomers. They can be made by the esterification of acrylic or methacrylic acid 40 with glycidol or with epichlorohydrin followed by dehydrohalogenation. The glycidyl group is capable of reacting with active methylene groups, with carboxylic acid groups and with other epoxide groups.

Polymerisable acid monomers used as component c) in the composition of this invention suitably are the well known mono or polycarboxylic acids which contain one polymerisable bond per molecule. Generally such acids will contain from 3 to 24 carbon atoms and one or two carboxylic acids groups per 45 molecule. Examples of such acids are acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, ethacrylic acid, crotonic acid, citraconic acid and half esters of the dicarboxylic acids wherein the esterified alcohol group contains from 1 to 20 carbon atoms. Examples of suitable half esters are methyl hydrogen fumarate, benzyl hydrogen maleate, butyl hydrogen maleate, octyl hydrogen itaconate and dodecyl hydrogen citraconate. The preferred acids for use in this invention are acrylic and methacrylic acid.

50 Any monomers which are copolymerisable with monomers a), b) and c) to provide a film-forming copolymer for use in the composition of the invention can be used as component d). Such monomers are those which contain no groups which are reactive under polymerisation conditions with acetoacetoxy groups, glycidyl groups or carboxylic acid groups.

The types and amounts of copolymerisable monomers d) will vary depending on the particular end use for which the product of this invention is intended. Such variations can be readily determined by those

skilled in the art.

Copolymerisable monomers which can be used as component d) are any of the well known monomers which contain one ethylenically unsaturated polymerisable group per molecule and are copolymerisable with the other monomers a), b) and c). Examples of such monomers are (meth)acrylic esters wherein the alcohol moiety contains 1 to 20 carbon atoms, e.g. methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, isopropyl acrylate, butyl acrylate, butyl methacrylate, 2-ethylhexyl methacrylate, decyl acrylate, lauryl methacrylate and benzyl acrylate.

Other (meth)acrylic esters which can be used to derive the copolymers are multifunctional (meth)acrylates, e.g. hexanediol diacrylate. Such esters can be used in amounts of, for example, up to 1 weight percent based on the total weight of the monomers.

Other copolymerisable monomers which can be used as component d) are vinyl aromatic monomers, such as styrene, vinyl toluene and alpha methyl styrene as well as nitriles and amides, e.g. acrylonitrile and acrylamide.

Still other copolymerisable monomers that can be used as component d) are derivatives of the hypothetical vinyl alcohol, for example, aliphatic vinyl esters such as vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate and the vinyl ester of Versatic acid.

Preferred comonomers for use as component (d) are the (meth)acrylate esters wherein the ester group is an alkyl group containing 1 to 8 carbon atoms.

The compositions of this invention are prepared by polymerisation of monomers a) to d) emulsified in water using conventional emulsion polymerisation procedures. Surfactants which can be used for emulsification of the monomers are anionic and nonionic surfactants and mixtures of anionic and nonionic surfactants.

Examples of useful anionic surfactants are organosulphates and sulphonates, e.g. sodium and potassium alkyl, aryl and alkaryl sulphates and sulphonates, such as sodium 2-ethylhexyl sulphate, potassium 2-ethylhexyl sulphate, sodium nonyl sulphate, sodium lauryl sulphate, potassium methylbenzene sulphonate, potassium toluene sulphonate and sodium xylene sulphonate; higher fatty alcohols, e.g. stearyl and lauryl, which have been ethoxylated and sulphonated; dialkyl esters of alkali metal sulposuccinic acid salts, such as sodium diamyl sulposuccinate, and sodium dioctyl sulposuccinate; formaldehyde-naphthalene sulphononic acid condensation products; alkali metal salts, partial alkali metal salts and free acids of complex organic phosphate esters.

Examples of nonionic surfactants which can be used are polyethers, e.g. ethylene oxide and propylene oxide condensates which include straight and branched chain alkyl and alkaryl polyethylene glycol and polypropylene glycol ethers and thioethers; alkylphenoxypoly(ethyleneoxy) ethanols having alkyl groups containing from about 7 to about 18 carbon atoms and having from 4 to 240 ethyleneoxy units, such as heptylphenoxy-poly(ethyleneoxy)-ethanols, nonylphenoxypoly(ethyleneoxy)ethanols; the polyoxyalkylene derivatives of hexitol (including sorbitans, sorbides, mannitans and mannides); partial long chain fatty acid esters, such as the polyoxyalkylene derivatives of sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate, sorbitan tristearate, sorbitan monooleate and sorbitan trioleate; the condensates of ethylene oxide with a hydrophobic base, said base being formed by condensing propylene oxide with propylene glycol; sulphur containing condensates, e.g. those prepared by condensing ethylene oxide with higher alkyl mercaptans, such as nonyl, dodecyl or tetradecyl mercaptan, or with alkylthiophenols wherein the alkyl group contains from 6 to 15 carbon atoms; ethylene oxide derivatives of long chain carboxylic acids, such as lauric, myristic, palmitic or oleic acids, or mixtures of acids, such as tall oil fatty acids; ethylene oxide derivatives of long chain alcohols such as octyl, decyl, lauryl or cetyl alcohols.

The amounts of surfactants employed in the emulsion polymerisation process generally range from 0.01 to 10 weight percent, preferably 0.2 to 5 weight percent based on the total weight of monomers and water.

In addition to the surfactants, the emulsion polymerisation system can also contain protective colloids. Examples of protective colloids are ether linkage-containing protective colloids, such as hydroxymethyl cellulose, hydroxyethyl cellulose, ethylhydroxyethyl cellulose, carboxymethyl cellulose and ethoxylated starch derivatives. Other protective colloid substances can also be used either alone or together with the ether linkage-containing materials. Other such protective colloids include partially and fully hydrolyzed polyvinyl alcohols, polyacrylic acid, sodium and other alkali metal polyacrylates, polyacrylamide, poly-(methyl vinyl ether/maleic anhydride), polyvinylpyrrolidone, water, soluble starch, glue, gelatin, water soluble alginates, such as sodium or potassium alginate, casein, agar and natural and synthetic gums, such as guar, gum arabic and gum tragacanth. The protective colloids can be used in the amounts ranging from 0.1 to 2 weight percent based on the total weight of the polymer emulsion.

The monomers a) to d) are suitably polymerised by means of a catalytic amount of a conventional free radical polymerisation catalyst or catalyst system (which can also be referred to as an addition poly-

merisation catalyst, a vinyl polymerisation catalyst, or a polymerisation initiator), preferably, although not necessarily, one which is substantially water soluble. Among such catalysts are peroxy compounds, such as hydrogen peroxide, tertiary butyl hydroperoxide and cumene hydroperoxide, alkali metal (e.g. sodium, potassium or lithium) and ammonium persulphates, perphosphates and perborates; azo nitriles, such as alpha, alpha-azobisisobutyronitrile, and redox systems including such combinations as mixtures of hydrogen peroxide or t-butyl hydroperoxide and any of the ferrous salts, titanous salts, zinc formaldehyde sulfoxylate, or sodium formaldehyde sulfoxylate; alkali metal or ammonium persulphate, perborate or perchlorate together with an alkali metal bisulphite, such as sodium metabisulphite; alkali metal persulphate together with an aryl phosphinic acid such as benzene phosphinic acid. The amount of polymerisation catalyst employed will be no more than that required to obtain substantially complete monomer conversion at low catalyst cost. The amount of catalyst will generally vary from 0.1 to 1 percent by weight based on the weight of the monomers.

The emulsification and polymerisation reaction can be conducted by any of the well known procedures which are used to prepare emulsion polymers. For instance, the monomers, catalyst, surfactants, protective colloids if used, and chain transfer agents, e.g. alkyl mercaptans, if used, can all be added to a reactor, and the reaction with suitable agitation to obtain emulsification, can be conducted at a temperature, for example, of 30° C to 95° C until the polymerisation is complete.

Alternatively, the reaction can be conducted by adding water, surfactants, and protective colloids, if used, into a reactor, raising the temperature to the reaction temperature and then adding the monomers and a solution of the catalyst to the reactor under agitation. Still another method is to pre-emulsify the monomers in a portion of the water and a portion of the surfactant along with catalyst, and to add the pre-emulsion to the reactor, which contains the remaining water and surfactant.

In order to obtain compositions which form coatings having superior coating properties when cured under ambient conditions, the acetoacetoxy moiety, the glycidyl moiety and the acid moiety must be present in certain preferred ratios. It has been found that acetoacetoxy group and the glycidyl group must be present in the weight ratio of less than or equal to 0.5/1 or greater than 1.5/1, wherein the weight ratios are calculated based on the weight of acetoacetoxyethyl (meth)acrylate a) and glycidyl (meth) acrylate b). The glycidyl group and the carboxylic acid group must be present in the weight ratio greater than 1.5/1 wherein the weight ratios are based on the weight of glycidyl (meth)acrylate b) and unsaturated acid c). Furthermore, the total weight percent of the monomers a), b) and c) in the copolymer is from 8 to 60 percent, said weight percents being based on the total weight of all monomers in the copolymer.

The amount of water used to prepare the compositions of this invention will depend upon the solids content desired in the finished copolymer emulsion. Generally the solids content will be from 20 to 70 weight percent, preferably 40 to 60 percent.

After the emulsion polymerisation is complete, the pH of the emulsion is adjusted to 8.5 to 10. This is suitably done using a water soluble base such as ammonia and alkali metal, ammonium and quaternary ammonium bases. Examples of suitable bases are ammonia, sodium hydroxide, potassium hydroxide, tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrabutylammonium hydroxide and benzyltrimethylammonium hydroxide. A particularly preferred base is tetramethylammonium hydroxide.

The polymer emulsion compositions of this invention can be applied to a variety of substrates to form films and coatings which cure at ambient temperatures.

The following Examples and Comparative Examples describe the invention in more detail. Parts and percentages are by weight unless otherwise indicated.

The extent of cure of the films in these examples was determined by testing for Gel Content and by calculating Swelling Index. These determinations were made on films which had been left under ambient conditions for at least 48 hours. The films were removed from the substrate and were tested as follows:

- (1) duplicate samples of the films, approximately 2 gram samples, were weighed into glass bottles;
- (2) toluene, 75 ml, was added to each bottle, the bottles were sealed and shaken vigorously;
- (3) after 3 days, the bottle contents were decanted onto a weighed fine nylon mesh screen, and were thoroughly washed with toluene;
- (4) the mesh screen was weighed, then dried in a vacuum oven and weighed; and
- (5) after determining the weight of wet gel and dry gel, the Gel Content and Swelling Index were determined as follows:

$$\% \text{ Gel Content} = \frac{\text{wt. of dry gel} \times 100}{\text{wt of film}}$$

$$\text{Swelling Index} = \frac{\text{wt wet gel} - \text{wt dry gel}}{\text{wt dry gel}}$$

Gel Contents of at least 96 percent and Swelling Indexes of 4 or less, preferably less than 3, indicate satisfactorily cured films.

Hot water resistance of the films was measured by immersing a weighed portion of dried polymer film in water at 80°C for 10 minutes. The percent water absorbed and the weight loss of the film were determined. The films were examined for blushing since water absorption does not always correlate with blushing. Cold water resistance was determined on films left in room temperature water for 7 days.

Example 1

To a suitable reactor fitted with two dropping funnels, condenser, agitator and thermometer, were added 355 parts of water, 1.95 parts sodium bicarbonate and 9.83 parts of phosphated nonyl phenyl polyethylene glycol ether surfactant. To one dropping funnel were added 111.45 parts of methylmethacrylate, 128.57 parts of butyl acrylate, 10 parts of acetoacetoxyethyl methacrylate, 7.5 parts of acrylic acid and 22.5 parts of glycidyl methacrylate. To the other dropping funnel were added 40.43 parts of water and 1.13 parts of ammonium peroxy disulphate. Agitation was begun and heat was applied raising the temperature in the reactor to 85°C. An initial charge of 0.06 part of ammonium peroxydisulphate in 19.5 parts of water was made to the reactor and the slow addition of monomers and catalyst was begun. While keeping the temperature at 85°C, the monomers were added over two hours and the catalyst over two hours and 5 minutes. The temperature was lowered to 70°C and 0.3 part of t-butylhydroperoxide was added. The temperature was then lowered to 35°C and a solution of 0.3 part of sodium formaldehyde sulfoxylate in 9.89 parts of water was added. When the temperature reached 25°C, 4.89 parts of 28 percent ammonium hydroxide and 1.18 parts of a microbiostat were added. The resulting stable latex had a viscosity of 0.025 Pas (25 cps), a solids content of 40.45 percent and a pH of 5.2.

The pH of a portion of the latex was adjusted with ammonia to 7.5 and then with sodium hydroxide to 9.0. (Example 1A). Another portion had the pH adjusted to 9.0 with tetramethylammonium hydroxide (Example 1B). Films were drawn down on glass panels and were left under ambient conditions for 48 hours. The films were removed from the substrate and tested with the results shown in Table 2.

Example 2

Using the same procedure described in Example 1, 143.76 parts of methyl methacrylate, 165.79 parts of butyl acrylate, 9.03 parts of methacrylic acid, 14.45 parts of acetoacetoxyethyl methacrylate and 28.9 parts of glycidyl methacrylate were polymerised. The resulting latex had a viscosity of 1.1 Pas (1100 cps) and a solids content of 47.32 percent. The pH of the latex was adjusted to 9.0 with tetramethyl ammonium hydroxide. Films were drawn down on glass panels and were left at ambient conditions for 48 hours. The film withstood 108 methyl ethyl ketone double rubs. The results of other film tests are shown in Table 2.

Example 3

Using the same procedure described in Example 1, a latex was made by polymerising 39.04 parts of

methyl methacrylate, 110.84 parts of butyl acrylate, 18.35 parts of methacrylic acid, 45.85 parts of acetoacetoxyethyl methacrylate and 91.76 parts of glycidyl methacrylate. The resulting latex had a viscosity of 0.015 Pas (15 cps) at 40.96 percent solids. The pH was adjusted to 8.5 with tetramethylammonium hydroxide. Films made from the latex were tested after drying for 48 hours under ambient conditions. Test results are shown in Table 2.

Comparative Example 1

Using the same procedure described in Example 1, a latex was made by polymerising 111.49 parts of methyl methacrylate, 128.57 parts of butyl acrylate, 5.02 parts of acrylic acid and 22.06 parts of acetoacetoxyethyl methacrylate. The latex had a viscosity of 0.0225 Pas (22.5 cps), a solids content of 39.88% and a pH of 7.38. The pH of the latex was adjusted to 7.5 with ammonia and to 9.0 with sodium hydroxide. Films made from the latex were tested after 48 hours under ambient conditions. The test results are shown in Table 2.

Comparative Example 2

Using the same procedure described in Example 1, a latex was made by polymerising 142.13 parts of methyl methacrylate, 163.87 parts of butyl acrylate, 6.4 parts of acrylic acid and 19 parts of glycidyl methacrylate. The latex had a viscosity of 0.1475 Pas (147.5 cps), a solids content of 45.74 percent and a pH of 7.4. The pH was adjusted to 9.0 with ammonia and sodium hydroxide. Films made from the latex were tested after 48 hours under ambient conditions. The test results are shown in Table 2.

Comparative Example 3

Using the same procedure described in Example 1, a latex was made using 145.8 parts of methyl methacrylate, 168.1 parts of butyl acrylate and 9.83 parts of acrylic acid. The latex had a viscosity of 1.65 Pas (1650 cps) and a solids content of 45.34 percent and a pH of 7.3. The pH of a portion of the latex was adjusted to 7.3 with ammonia. Another portion had the pH adjusted to 9.0 with tetramethylammonium hydroxide (TMAH). Films made from the latex were tested after 48 hours at ambient conditions. The film made from the portion containing TMAH withstood 38 methyl ethyl ketone double rubs. The test results are shown in Table 2.

Comparative Example 4

Using the same procedure described in Example 1, a latex was made by polymerising 153.11 parts of methyl methacrylate, 176.47 parts of butyl acrylate, 10.87 parts of acetoacetoxyethyl methacrylate and 21.73 parts of glycidyl methacrylate. The latex had a viscosity of 0.075 Pas (75 cps) and a solids content of 39.88 percent. The pH of the latex was adjusted to 9.0 with tetramethylammonium hydroxide. Films made from the latex were tested after drying for 48 hours under ambient conditions. The test results are shown in Table 2.

Comparative Example 5

Using the same procedure described in Example 1, a latex was made by polymerising 120 parts of methyl methacrylate, 138.74 parts of butyl acrylate and 8 parts of acrylic acid. The latex had a viscosity of 0.020 Pas (20 cps) and a solids content of 40.38 percent. The pH was adjusted to 8.5 with tetramethylammonium hydroxide. Films made from the latex were tested after drying for 48 hours under ambient

conditions. The test results are shown in Table 2.

Comparative Example 6

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Using the same procedure described in Example 1, 111.49 parts of methylmethacrylate, 128.57 parts butyl acrylate, 5.01 parts of acrylic acid, 7.42 parts of acetoacetoxyethyl methacrylate and 10.2 parts of glycidyl methacrylate were polymerised. The resulting latex had a viscosity of 0.0275 Pas (27.5 cps), a solids content of 40.74 percent and a pH of 7.45. The pH of the latex was adjusted to 7.5 with ammonia and to 9.0 with sodium hydroxide. Films made from the latex were tested after 48 hours under ambient conditions. The test results are shown in Table 2.

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Table 1

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Example (Ex) or Comparative Example (C.Ex)	Monomer Content			
	AAEM wt %	GMA wt %	MAA/AA wt %	Other Monomer wt %
Ex 1	3.5	8	2.5	86
Ex 2	4	8	2.5	85.5
Ex 3	15	30	6	49
C. Ex 1	8	-	2	90
C. Ex 2	-	6	2	92
C. Ex 3	-	-	3	97
C. Ex 4	3	6	-	91
C. Ex 5	-	-	3	97
C. Ex 6	3	4	2	91
AAEM - acetoacetoxyethyl methacrylate GMA - glycidyl methacrylate MAA - methacrylic acid AA - acrylic acid				

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Table 2

Ex. or C. Ex.	Gel Content wt %	Swelling Index	Tensile MPa (psi)	Elong. %	Hot Water Abs %	Wt Loss wt %	Film Blush	Cold Water Abs %	Wt Loss %	Film Blush
Ex 1A	96.13	4.02	7.922(1149)	182	29.08	2.51	No	13.87	2.54	No
Ex 1B	96.34	2.98	7.026(1019)	173	6.78	3.69	No	8.12	5.21	No
Ex 2	97.5	2.58	10.90 (1581)	123	8.91	0.92	No	8.92	1.99	No
Ex 3	97.2	1.04	15.17 (2200)	5	1.79	4.73	No	1.95	6.19	No
C. Ex 1	91.2	8.39	6.48 (940)	265	25.44	0.53	Yes	-	-	
C. Ex 2	92.31	8.2	7.708(1118)	239	12.76	2.89	No	-	-	
C. Ex 3*	83.82	28.66	6.01 (871)	376	17.30	1.62	Neg.	90.0	2.7	Yes
C. Ex 3**	79.75	30.56	2.65 (384)	475	89.98	9.11	Yes	124.87	5.06	Yes
C. Ex 3***	97.08	3.03	9.191(1333)	143	20.31	0.49	Yes	7.0	1.5	No
C. Ex 4	88.28	8.47	5.40 (783)	317	14.64	0.9		47.12	0.54	
C. Ex 5	79.75	30.56	2.65 (384)	475	89.98	9.11	Yes	124.87	5.06	Yes
C. Ex 6	95.09	6.61	5.61 (814)	277	13.99	0	No	-	-	No

* C. Ex 3 neutralised with ammonia - pH 7.3

** C. Ex 3 neutralised with TMAH - pH 9.0

*** C. Ex 3 blended with polyaziridine - (2% W/W) - Xama 7 from Sannacor Industries.

Claims

1. A coating composition which comprises an aqueous dispersion having a pH of 8.5 to 10 of a copolymer of a) acetoacetoxyethyl acrylate or methacrylate, b) glycidyl acrylate or methacrylate, c) an ethylenically unsaturated polymerisable acid, and d) a monomer other than a), b) and c) and copolymerisable therewith, wherein the weight ratio a) to b) is less than or equal to 0.5/1 or greater than 1.5/1 and the weight ratio of b) to c) is greater than 1.5/1, the total weight percent of a), b) and c) in the copolymer is from 8 to 60, the weight percent of c) is from 1.5 to 20 and the weight percent of d) is from 40 to 92.
2. A composition according to claim 1 wherein the ethylenically unsaturated polymerisable acid c) is acrylic acid or methacrylic acid.
3. A composition according to claim 1 or 2 wherein the copolymerisable monomer d) is a C₁-C₈ alkyl acrylate or methacrylate.
4. A composition according to claim 3 wherein the copolymerisable monomer d) is methyl methacrylate or butyl acrylate.
5. A composition according to any one of the preceding claims wherein the pH has been adjusted with a water soluble base.
6. A composition according to claim 5 wherein the base is ammonia, sodium hydroxide or a quaternary ammonium hydroxide.
7. A composition according to claim 6 wherein the quaternary ammonium hydroxide is tetramethylammonium hydroxide.



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European Patent Office
Office européen des brevets



Publication number:

0 372 804 A3

12

EUROPEAN PATENT APPLICATION

21 Application number: 89312390.1

22 Date of filing: 29.11.89

51 Int. Cl.⁵: C09D 133/14, C08F 220/28,
/(C08F220/28,220:32,220:06,
220:10)

30 Priority: 09.12.88 US 281652

43 Date of publication of application:
13.06.90 Bulletin 90/24

64 Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

66 Date of deferred publication of the search report:
23.10.91 Bulletin 91/43

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54 Ambient temperature curing polymer compositions.

57 The invention relates to a coating composition which cures at ambient temperatures which comprises an aqueous dispersion having a pH of 8.5 to 10 of a copolymer of a) acetoacetoxyethyl acrylate or methacrylate, b) glycidyl acrylate or methacrylate, c) an ethylenically unsaturated polymerisable acid, and d) a monomer other than a), b) and c) and copolymerisable therewith, wherein the weight ratio a) to b) is less than or equal to 0.5/1 or greater than 1.5/1 and the weight ratio of b) to c) is greater than 1.5/1, the total weight percent of a), b) and c) in the copolymer is from 8 to 60, the weight percent of c) is from 1.5 to 20 and the weight percent of d) is from 40 to 92.

EP 0 372 804 A3



European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 31 2390

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,A	EP-A-0 326 723 (ROHM AND HAAS CO.) * Page 17, line 8; page 20, line 20 * & ZA-A-8 800 725 (ROHM AND HAAS CO.) (Cat. A) -----	1	C 09 D 133/14 C 08 F 220/28 // (C 08 F 220/28 C 08 F 220:32 C 08 F 220:06 C 08 F 220:10)
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 09 D C 08 L C 08 F
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of search 25 July 91	Examiner SCHUELER D.H.H.
<div>CATEGORY OF CITED DOCUMENTS</div> <div>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention</div> <div>E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons</div> <div>&: member of the same patent family, corresponding document</div>			